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Reorganization Free Energy for Electron Transfers at Liquid-Liquid and Dielectric Semiconductor-Liquid Interfaces

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Abstract

The reorganization free energy is calculated for a reaction between (*i*) two reactants, each in its own dielectric medium, separated by an interface, and (*ii*) between a reactant and some semiconductors. An expression is also given for the rate constant of an electron transfer reaction at an interface between reactants in two immiscible phases. Under certain conditions it is shown that the reorganization energy for the two-immiscible liquid system is the sum of the electrochemical reorganization energies of the two reactants, each in its own respective solvent. The reorganization energy for a semiconductor/liquid system can differ considerably from the corresponding metal/liquid value, even a factor of two.

Contribution No. 8006

Introduction

Some time ago I derived an expression for the reorganizational free energy λ in electron transfer reactions occurring in homogeneous solutions[1-3] and at metal-solution interfaces.[3-5] Since that time there have also been studies on electron transfers at liquid-liquid interfaces[6-9] and at semiconductor-liquid interfaces.[10-12] In the present paper we obtain expressions for the reorganization free energy at such interfaces, using the same approximations as those used earlier.[3] In the case of a metal-liquid surface, whose results [3-5] are given for comparison (eq. (11), below), the detailed electronic structure properties[13,14] of the metal surface are neglected and a local dielectric response is used for the liquid.[15]

Earlier, using a charging path to produce a system with a nonequilibrium dielectric polarization, we obtained a classical statistical mechanical expression for the free energy of a system having longitudinal polarization fluctuations.[16] This result was then expressed in terms of the free energies of certain hypothetical equilibrium systems,[16] and proved convenient for deriving expressions for reorganization free energy,[3] as well as for obtaining other properties, such as spectral shifts in polar media for simple and less simple (e.g., ellipsoidal) solute shapes.[17] The principal assumptions used were (1) linearity of the response of the medium to a change in electric field, (2) a static treatment of the low-frequency motions, and (3) instantaneous response of the electronic polarization in the system to a change in electric field. We also comment on the applicability of the relation to systems with linear but nonlocal dielectric response.

Theory

We consider a nonequilibrium system having some charge distribution, denoted by ρ_1, in an environment which would be in equilibrium with a different charge distribution ρ_0. Expressed in terms of equilibrium free energies, the free energy of formation $G_1^{non} - G_1^{e}$ of this nonequilibrium system from a similar system, but one which is in thermal equilibrium, is given by eq. (15) of ref. 16:

$$G_1^{non} - G_1^e = G_{1-0}^{e,op} - G_{1-0}^e \ , \tag{1}$$

where G_1^e is the free energy of the equilibrium system with charge distribution ρ_1, $G^e{}_{1-0}$ is that of an equilibrium system with a hypothetical charge distribution $\rho_1 - \rho_0$, and $G^{e,op}{}_{1-0}$ is the corresponding quantity when only an electronic response of the medium or media to the charge occurs. (In the last case, any dielectric constant would be replaced by the optical dielectric constant.) All quantities in eq. (1) are calculated at a fixed position of the reactant(s).

While statistical mechanical expressions can be introduced in the RHS of eq. (1) we employ here the dielectric continuum expressions. We first consider the case of two dielectrics having a plane interface at $z=0$, z being the coordinate normal to the interface. A charge q is fixed at a distance d from the interface in the liquid labelled 1, which occupies the region $z > 0$. The static and optical dielectric constants are denoted by D_i^s and D_i^{op}, i indicating the phase ($i=1$ for $z>0$, $i=2$ for $z<0$). The electrostatic potential ψ satisfies several boundary conditions at the interface:[18]

$$\begin{aligned} \lim_{z\to 0^+} D_1\, \partial\psi/\partial z &= \lim_{z\to 0^-} D_2\, \partial\psi/\partial z \\ \lim_{z\to 0^+} \partial\psi/\partial x &= \lim_{z\to 0^-} \partial\psi/\partial x \\ \lim_{z\to 0^+} \partial\psi/\partial y &= \lim_{z\to 0^-} \partial\psi/\partial y \quad , \end{aligned} \tag{2}$$

where x and y are coordinates parallel to the planar interface

The present results are obtained for infinite dilution, in the case of any liquid phase, although work terms to reach the interface in the presence of added electrolyte can be included.[19] To include an ion atmosphere reorganization term eq. (1) can still be used, as in ref. 3, when the response of an ion atmosphere to a change in charge is in the linear regime. In the case of a semiconductor-liquid system the semiconductor is treated here for simplicity as undoped, or as having a small enough concentration of electrons and holes that eqs. (3) and (4) below remain valid in the interfacial region. We expect to treat other systems later.

The expression for ψ at any field point (x, y, z), denoted by P, is given by (3) and (4) when these boundary conditions are satisfied:[18]

$$\psi(x,y,z) = \frac{q}{D_1}\left[\frac{1}{R_1} - \frac{D_2-D_1}{(D_2+D_1)R_1'}\right], \quad z>0 \tag{3}$$

and

$$\psi(x,y,z) = \frac{2q}{(D_1+D_2)R_1}, \quad z<0 \tag{4}$$

Here, R_1 is the distance from the ion to the field point P, R_1' is the distance to P from the electrostatic image of the ion. The image lies at the same x and y as the ion but at $z=-d$.

If we consider an ion of radius a, the electrostatic potential ψ acting on this ion surface is obtained[20] by setting $R_1=a$ and $R_1'=R$ in eq. (3), R being the distance between the center of the ion and its image. Thus, $R=2d$, and so is twice the distance to the interface. The free energy G^e is then obtained by charging the ion from $q=0$ to $q=q$, calculating $\int\psi\, dq$, and subtracting the corresponding quantity at $R=\infty$ in a vacuum $(D_1=D_2=1)$. We thus obtain, for this equilibrium system,

$$G^e = \frac{q^2}{2D_1}\left[\frac{1}{a} - \frac{D_2-D_1}{(D_2+D_1)R}\right] - \frac{q^2}{2a} . \tag{5}$$

In a treatment of electron transfer reactions, in which an ion (or molecule) has a charge e^r before the electron transfer and a charge e^p after, (and there could be several such ions, $e^r{}_j \rightarrow e^p{}_j$, $j=1,2$, for example) the charge which determines the distribution of coordinates in the transition state $e^\ddagger$ was shown earlier to be given by[1-3]

$$e^\ddagger = e^r + m(e^r - e^p) , \tag{6}$$

where m is a Lagrangian parameter; m is determined from the thermodynamic properties of the system, e.g., eq. (79) of ref. 3 for a homogeneous reaction, eq. (80) for a reaction at a metal-solution interface, or from related equations which can be derived for the other systems. (We give eq. (79) later.) Thus, the charge distribution $\rho_1 - \rho_0$ in eq. (1) corresponds to a charge $e^{\ddagger} - e^r$ and hence to $m(e^r - e^p)$.

We then obtain at a fixed position of the reactant,[2,3]

$$G_1^{non} - G_1^e = m^2\lambda = m^2(\lambda_0 + \lambda_i) \quad , \tag{7}$$

where λ_i is any vibrational contribution from the reactants, due to changes in the equilibrium values of their vibrational coordinates[2,3] due to the reaction; λ_i is given by eq. (9) below, and λ_0 is given by

$$\lambda_0 = \frac{(\Delta e)^2}{2a}\left(\frac{1}{D_1^{op}} - \frac{1}{D_1^s}\right) - \frac{(\Delta e)^2}{2R}\left(\frac{D_2^{op} - D_1^{op}}{D_2^{op} + D_1^{op}}\,\frac{1}{D_1^{op}} - \frac{D_2^s - D_1^s}{D_2^s + D_1^s}\,\frac{1}{D_1^s}\right) , \qquad (R = 2d) \tag{8}$$

where $\Delta e = e^r - e^p$.

The reorganizational parameter λ_i can be written[2,3] in terms of the displacements $q_{0j}{}^r - q_{0j}{}^p$ of the equilibrium values of the normal vibrational coordinates and the "reduced" normal mode force constants k_j,

$$\lambda_i = \tfrac{1}{2}\sum_j k_j\,(q_{0j}^r - q_{0j}^p)^2 \quad , \tag{9}$$

when a reactant has the same vibrational symmetry in the initial (r) and final (p) state. The sum is over all normal coordinates of the single reactant in the above case and of the pair of reactants in the next case. The k_j is related to the normal mode force constants before (k_j^r) and after (k_j^p) reaction by [3]

$$k_j = 2k_j^r k_j^p / (k_j^r + k_j^p) \quad . \tag{10}$$

Normal mode force constants appear in eq. (9). A use of purely diagonal bondstretching force constants has been shown to lead to considerable error,[21] when the bond-bond cross-terms are not small.

Equation (8) was derived for the case of two dielectric media. It is useful to see what it reduces to in the case where phase 2 is a classical metallic conductor. In this limit both D_2's are replaced by infinity and eq. (7) becomes

$$\lambda_o = \frac{(\Delta e)^2}{2}\left(\frac{1}{D_1^{op}} - \frac{1}{D_1^{s}}\right)\left(\frac{1}{a} - \frac{1}{R}\right), \qquad (R=2d) \tag{11}$$

an expression obtained earlier.[3-5]

We consider next the case where there are two reactants, one in each phase. The electrostatic potential arising from ions 1 and 2 is now given by the sum of two terms: For $z>0$, these terms arise from eq. (3) for ion 1, by setting $q=q_1$. The second contribution for $z>0$ comes from ion 2, and can be obtained from eq. (4) by setting $q=q_2$ there and replacing R_1 by R_2, the distance from ion 2 to the field point P:

$$\psi(x,y,z) = \frac{q_1}{D_1}\left(\frac{1}{R_1} - \frac{D_2-D_1}{(D_2+D_1)R_1'}\right) + \frac{2q_2}{(D_1+D_2)R_2} \qquad (z>0)\ . \tag{12}$$

Similarly, ψ for $z<0$, is obtained by interchanging the 1 and 2 symbols:

$$\psi(x,y,z) = \frac{q_2}{D_2}\left(\frac{1}{R_2} - \frac{D_1-D_2}{(D_1+D_2)R_2'}\right) + \frac{2q_1}{(D_1+D_2)R_1} \qquad (z<0)\ . \tag{13}$$

The relevant potential ψ_1 used in the charging of ion 1 is obtained from eq. (12) by setting[19] $R_1=a_1$, $R_2=R$, and $R_1'=2d_1$, where d_1 is the distance from the center of ion 1 to the interface. The relevant potential ψ_2 used in the simultaneous charging of ion 2 is obtained from (13) by setting there $R_2=a_2$, $R_1=R$, and $R_2'=2d_2$.

To obtain a free energy, $\psi_1 dq_1 + \psi_2 dq_2$ is integrated from $q_1=0$ to q_1 and from $q_2=0$ to q_2, by setting $q_1=\gamma q_1$, $q_2=\gamma q_2$ and integrating over γ from 0 to 1. To obtain G^e, the corresponding quantity at $R=\infty$ for a vacuum is subtracted. We then have

$$G^e = \frac{q_1^2}{2a_1}\left(\frac{1}{D_1}-1\right) + \frac{q_2^2}{2a_2}\left(\frac{1}{D_2}-1\right) - \left(\frac{q_1^2}{4d_1D_1} - \frac{q_2^2}{4d_2D_2}\right)\frac{(D_2-D_1)}{(D_2+D_1)} + \frac{2q_2q_1}{R(D_1+D_2)} \quad (14)$$

Replacing q_1 by $m(e_1{}^r - e_1{}^p) \equiv -m\Delta e$, q_2 by $m(e_2{}^r - e_2{}^p) \equiv +m\Delta e$ and then using eq. (1) we have, at fixed position of the two reactants,

$$G^{non} - G^e = m^2\lambda = m^2(\lambda_0 + \lambda_i) \ , \quad (15)$$

where λ_i is given by eqs. (9) and (10) and where

$$\lambda_0 = \frac{(\Delta e)^2}{2a_1}\left(\frac{1}{D_1^{op}} - \frac{1}{D_1^s}\right) + \frac{(\Delta e)^2}{2a_2}\left(\frac{1}{D_2^{op}} - \frac{1}{D_2^s}\right) - \frac{(\Delta e)^2}{4d_1}\left(\frac{D_2^{op}-D_1^{op}}{D_1^{op}(D_2^{op}+D_1^{op})} - \frac{D_2^s - D_1^s}{D_1^s(D_2^s+D_1^s)}\right)$$

$$- \frac{(\Delta e)^2}{4d_2}\left(\frac{D_1^{op}-D_2^{op}}{D_2^{op}(D_1^{op}+D_2^{op})} - \frac{D_1^s - D_2^s}{D_2^s(D_1^s+D_2^s)}\right) - \frac{2(\Delta e)^2}{R}\left(\frac{1}{D_1^{op}+D_2^{op}} - \frac{1}{D_1^s+D_2^s}\right) . \quad (16)$$

When the two media are identical ($D_1{}^s = D_2{}^s \equiv D^s$, $D_1{}^{op} = D_2{}^{op} \equiv D^{op}$) eq. (16) reduces to an expression obtained earlier:[1]

$$\lambda_0 = (\Delta e)^2\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R}\right)\left(\frac{1}{D^{op}} - \frac{1}{D^s}\right) . \quad (17)$$

In an electron transfer reaction one also needs to have[1-5], when the reactants approach each other from R = ∞, the corresponding work term w^r and the work term $-w^p$ to remove the products to R = ∞. The free energy barrier to reaction $\Delta G_r^\ddagger$ is then given by[1-5],

$$\Delta G_r^\ddagger = w^r + m^2\lambda \ . \quad (18)$$

In the case of a homogeneous reaction the Lagrangian multiplier m satisfies the equation[1-5]

$$-(2m+1)\lambda = \Delta G^{0'} + w^p - w^r \quad , \tag{19}$$

where $\Delta G^{0'}$ is the "standard" free energy of reaction in the prevailing medium. In the case of an electrochemical reaction, m is given by the electrochemical analog of eq. (19) (e.g., for a metal electrode eq. (80) of ref. 3).

A dielectric continuum expression for w^r at infinite dilution for the system can be obtained by subtracting from the G^e for reactants 1 and 2, the value for G^e when they are far from the interface. At infinite dilution, this result for w^r is then found from eq. (14) to be

$$w^r = -\left(\frac{(e_1^r)^2}{4d_1 D_1^s} - \frac{(e_2^r)^2}{4d_2 D_2^s} \right)\left(\frac{D_2^s - D_1^s}{D_2^s + D_1^s} \right) + \frac{2}{R} \; \frac{e_1^r e_2^r}{(D_1^s + D_2^s)} \quad . \tag{20}$$

Similarly, w^p is obtained by replacing each charge e_i^r by the corresponding value for the products, e_i^p. In practice, more elaborate expressions for w^r and w^p are more appropriate, because of solvent structure-breaking and structure-forming effects of the ions, in addition to any electrolyte effects on w^r and w^p.[19]

We have treated the metal in the metal-liquid system as a classical conductor.[3,4] For the sake of completeness we note here some recent work on electronic structure effects on the calculated electrostatic image potential. There are many quantum mechanical studies of the forces between a charge and a metal,[13] designed in part to treat experimental data on work functions, LEED, and other topics. For distances greater than about 3 Å the interaction energy G^e of an electron and the surfaces is approximated by[13]

$$G^e = -\frac{e^2}{4(d-d_0)} \qquad (d>3\text{ Å}) \tag{21}$$

where d is the distance from the charge to the solid surface[22] and d_0 is a small quantity for which estimates have been made.[22] To fit some LEED intensity line shapes eq. (21) for $d>3$ Å was joined linearly to a given value at $d=0$.[22b] An alternative model, described as hydrodynamic and phenomenological, gave even smaller corrections to the classical image charge formula.[23]

From eq. (21) the electrostatic potential ψ_{ion} due to the image acting on the charge is

$$\psi = -\frac{q}{2(d-d_0)} \qquad (d > 3\text{ Å}) \quad . \tag{22}$$

In a nonlocal treatment of the metal, Dzhavakhidze *et al.*[24] used a Thomas-Fermi screening approximation for the wave number k dependence of the dielectric constant of the metal

$$D_M^S = D_M(1 + k_s^2/k^2) \quad , \tag{23}$$

where k_s^{-1} is the Thomas-Fermi screening length ($\sim$0.5 Å) and $D_M \sim 1$ to 2. Results were obtained for λ_0 for the metal-liquid interface, both for the case of a local dielectric response of the solvent and for a nonlocal response with an exponential decay on separation distance. In the former instance λ_0 was given by

$$\lambda_0 = \frac{(\Delta e)^2}{2}\left(\frac{1}{a} - \frac{1}{R}f(Rk_sD_M/D^s)\right)\left(\frac{1}{D^{op}} - \frac{1}{D^s}\right) \qquad (R \gg 2k_s^{-1}) \tag{24}$$

where $f(x)$ is a known function which tends to unity when $x \to \infty$ (it is fairly close to unity for $x \sim 3$) and which passes through zero at $x \sim 0.25$ and then becomes negative for smaller x. It would appear that this type of treatment would also lead to an image repulsion of an approaching ion in solution, instead of image attraction, when $Rk_sD_M/D^s < 0.25$. Such a result might be capable of direct experimental test. It would also be useful to explore this question further theoretically, using instead the type of treatment of the metal surface given in ref. 13, which is more rigorous than phenomenological ones such as that in ref. 14.

Reaction Rate Constant

(*i*) *Two Immiscible Phases*

We calculate first a rate constant k_r for reaction between two reactants, one in each of the two immiscible phases. Its units can be defined via[25]

$$-\frac{dN_1}{dt} = k_r n_1 n_2 A \quad , \tag{25}$$

where N_1 is the number of molecules of type 1 in phase 1, n_1 is the mean concentration of reactant 1 in phase 1, n_2 is the mean concentration of reactant 2 in phase 2 and A is the interfacial area. The units of k_r are seen to be cm^4 molecule^{-1} sec^{-1}. We let υ (determined below) be a "volume" (units of cm^4) such that in a unit area of interface the center-to-center distance of the pair of reactants lies in $(R, R+\Delta R)$, where ΔR, defined in the Appendix, is the region over which there is a significant contribution to the ET process, and where reactant 1 lies wholly in phase 1 and reactant 2 in phase 2. If κ is some Landau-Zener factor[26] for the ET in this region of R and ν is some relevant frequency for the molecular motion then k_r can be written, approximately, as

$$k_r = \kappa \nu \upsilon e^{-\Delta G_r^{\ddagger}/k_B T} , \tag{26}$$

where $\Delta G_r^{\ddagger}$ is given by eqs. (18) and (19). The terms w^r and w^p in those equations now denote the work required to bring the reactants (w^r) and the products (w^p) from $R = \infty$ to a mean reactive separation distance $R^{\ddagger}(\simeq a_1 + a_2)$. Such work terms may include not only that in eq. (20) but, as already noted, other effects.

In the Appendix it is shown that the leading term in an expression for an effective υ is

$$\upsilon = 2\pi (a_1 + a_2)(\Delta R)^3 \tag{27}$$

when a sharp boundary at the interface is assumed.

When the two phases are "immiscible" liquids some interpenetration of the two phases may occur, so that the reactants may then be able to approach each other over a wider solid angle than that indicated in Fig. 1. For example, if the centers of ions 1 could each penetrate the other phase to the extent that each center could even reach the interfacial boundary, but such that the reactants wouldn't overlap one would obtain (Appendix A) eq. (28) instead of eq. (27).

$$\upsilon \sim \pi (a_1 + a_2)^3 \Delta R \tag{28}$$

The rate of electron transfer typically decays with distance as exp $(-\beta R)$, (some data are summarized in ref. 27) and $\Delta R = 1/\beta$ (Appendix). Using a value of $\beta \sim 1$ Å^{-1}, ΔR is about 1 Å. When $a_1 + a_2 \sim 5$ Å, the υ in eq. (28) is then about a factor of ten larger than that in eq. (27). A molecular investigation of the interface and of the extent of interpenetration of the reactants in the two-liquid case would be desirable. We plan to compare elsewhere the above results for υ, and those given earlier for λ, with some available data on rate constants. Equation (16) for λ_0 is restricted, of course, to the case when there is no interpenetration. If only one of the two ions can interpenetrate, υ has a value intermediate between that in eq. (27) and in eq. (28).

(*ii*) *Comment on Semiconductor-Solution Electron Transfers*

Equations (18) and an electrochemical analog of eq. (19) have been applied to electron transfers at semiconductor electrodes, typically with λ regarded as a parameter.[11] A general λ includes[3] the reorganization of the solvent dielectric polarization, of the vibrational coordinates, of the ion atmosphere in solution, and depending on the system, of the electron and hole distributions in the semiconductor.

One question which arises is the rapidity of response of the electronic and hole charge distribution in the semiconductor to an actual fairly abrupt electron transfer with the reactant. A characteristic time for that transition τ can be inferred from the Landau-Zener-type expression for the probability P of a radiationless transition in the following way: For an electron transfer at a "crossing" of the potential energy surfaces for the electron transfer we have [3,26]

$$P = 1 - e^{-\frac{2\pi}{\hbar}\frac{H_{12}^2}{|s_1 - s_2|\,v_x}}, \qquad (29)$$

where H_{12} is the absolute value of the electronic matrix element for the electron transfer and v_x is the velocity at the crossing.

To answer the question regarding response time it is useful to recast eq. (29), as in eq. (30). The time for a nonstationary state of the reactant, at the curve crossing, to undergo a charge transfer between the two nearly degenerate electronic states there is $\Delta t = \hbar\pi/2H_{12}$, using a standard quantum mechanical analysis.[28] Equation (29) can be rewritten suggestively in the form (30), using this Δt.

$$P = 1 - e^{-\tau/\Delta t}\ , \quad \Delta t = \hbar\pi/2H_{12}\ , \tag{30}$$

where τ is, effectively, the time spent by the system in the crossing region; τ is defined by a comparison of eqs. (29) and (30) to be

$$\tau = \pi^2 H_{12}/v_x|s_1 - s_2|\ . \tag{31}$$

An interpretation of eq. (30) is that the system passes through the intersection region in a time $\sim\tau$. When this time τ is small relative to the time Δt for the change of the reactant's charge, there is only a small probability of the electron transfer occurring on a passage through the crossing region, as seen, for example, in eq. (30).

With a little manipulation, using a vibrational coordinate as the reaction coordinate, with a vibration frequency ν, and, for the present, replacing the velocity v_x by an average value one finds[29]

$$\tau \sim H_{12}/\nu(\lambda_i k_B T)^{\frac{1}{2}}\ . \tag{32}$$

Thus, the smaller the electronic interaction energy H_{12} the shorter the time τ spent by the system in the vicinity of the potential energy curve crossing.

Depending on the ratio of this time scale τ to the time scale for the relaxation of the electron (or hole) charge distribution in the semiconductor, the latter may act as a dielectric. For example, if τ is relatively small, then eqs. (9) and (16) may be appropriate for λ_0. At the other limit, the response in the semiconductor may be rapid enough, and the shielding large enough, that it can be treated as a metal and eq. (11) is obtained in this limit.

A helpful discussion and survey of the theory of electron transfer at semiconductors, and the role of λ is given in ref. 11. We hope to return to this topic at a later date.

Discussion

(*i*) *Two Immiscible Liquid Interface*

An interesting consequence of eq. (16) is that when $D_1^{op} = D_2^{op}$ and $d_1 = d_2 = \frac{1}{2}R$, the λ_0 in (16) is the sum of the two electrochemical λ_0's (eq. (11)), each ion being in its own respective solvent:

$$\lambda_0 \simeq \lambda_{0,1}^{el} + \lambda_{0,2}^{el} \tag{33}$$

We plan to apply this result elsewhere.

There are both similaries and differences between eq. (16) and the corresponding equations in ref. 6. The $1/a_1$ and $1/a_2$ terms are the same [e.g., eq. (4) of ref. 6b]. The remaining part of (16) differs, though it and the corresponding terms in ref. 6 become equal in some particular cases. The results in eq. (20) for w^r and w^p are the same as those in ref. 6 (eqs. (5)-(7) of ref. 6b), when eq. (20) is specialized to the case where the line of centers of the two reactants is normal to the interface (i.e., when $R = d_1 + d_2$).

(*ii*) *"Undoped" Semiconductor-Liquid Interface*

As an example of eqs. (8) and (11) we compare them for the case that $D_1^{op} = D_2^{op} = 2$, $D_1^s = 10$ (semiconductor) and $D_2^s = 40$. In this case and with $R \simeq 2a$, the λ_0 in eq. (8) has about twice the value as that in eq. (11). The reason for this large effect is that in the metal-liquid case the image charge tends to reduce the effect of the approaching charge on the solvent polarization, whereas in a semiconductor (D_2^s)/liquid (D_1^s) system it concentrates the effect of the charge in medium 1, when $D_2^s < D_1^s$, and hence increases the amount of reorganization needed.

(*iii*) *Metal-Electrolyte* λ_0

The results in ref. 3 appear to be consistent with a comparison of some homogeneous and heterogeneous (metal electrode) electron transfer rate constants, a log-log plot of which appears to have a slope of roughly 0.5,[30,31] although the scatter makes the slope somewhat uncertain. The homogeneous solution k's varied by some twenty orders of magnitude. In these systems the λ_i is, no doubt, non-negligible and λ_i for a homogeneous (self-exchange) reaction is twice that for the heterogeneous one at the metal electrodes,[3] and so helps preserve a slope of roughly 0.5. The slope is predicted[3,27,32] to be between 0.5 and 1, depending on whether or not there is a layer of solvent molecules on the electrode surface which prevents the ion from having $R = 2a$, and depending, too, on the contribution of λ_i to λ. This slope of 0.5 does differ from that predicted theoretically in ref. 24, for which a very large slope of 1.9 to 2.4 was suggested for acetonitrile on the basis of nonlocal dielectric response calculations. The slope predicted[30] on similar grounds for dimethyl formamide as solvent was 0.7. The predicted slope (e.g., in Figs. 5 and 6 in ref. 24) was not given for water. No λ_i term was included there, since the focus was on λ_0. An experimental comparison of corresponding self-exchange homogeneous and electrochemical rate constants in acetonitrile as solvent, suitably corrected for work terms, would be useful as a test of this rather surprising nonlocal electrostatics prediction of ref. 24.

The interpretation of homogeneous vs. electrochemical data where λ_i is small is currently under active investigation. Both solvent static and dynamic effects occur, and for these fast reactions (small λ_i) the variation in k's was not very large. The most recent analysis of the data is that given in ref. 33, which illustrates some of the complexities.

(*iv*) *Nonlocal Dielectric Response*

We have not treated in the present paper any nonlocal dielectric effects[34,35] in the liquid. These and other effects such as short range specific interactions no doubt occur. Apparently there is, as yet, no direct experimental measurement of nonlocal dielectric response parameter for polar solvents (e.g., a determination of an orientational analog of the slow neutron scattering-determined structure factor). Results for the nonlocal dielectric response would be obtainable from suitable molecular dynamics (MD) computer simulations of a statistical mechanical system, though such results would be only as good as the molecular model used in the calculation. Such effects are physically different from specific short range electrode-solvent and ion-solvent interactions. To distinguish them from the latter, the nonlocal dielectric effects are presumably best investigated in MD simulations of the ion-free and interface-free solvents. Attempts to infer them[36] from experimental data at interfaces or from data on ion-solvent interactions encounter the problem of disentangling those effects from the other short-range effects, dielectric saturation, for example, or various specific effects.[37,38] One alternative has been to include all such effects phenomenologically into one or more parameters,[39] which are then adjusted to best fit some data.

The derivation of eq. (1) given in ref. 16 was based on rather general linear functional type arguments and might be expected to apply, therefore, to nonlocal response dielectrics also. (This derivation of eq. (1) was more general than a dielectric continuum-based derivation,[40] which did assume a local dielectric response.) Recently, we have made a continuum-based derivation using a nonlocal response for single phase systems and eq. (1) was again obtained.[41] For the case where there is more than one phase some assumption for the nonlocal dielectric constant $\varepsilon(\mathbf{r}, \mathbf{r}')$ in the vicinity of the interface is needed. One assumption in the literature, a "specular electron reflection ansatz", is that it correlates only points $\mathbf{r}$, $\mathbf{r}'$ in the same phase and is zero otherwise.[42,43] This approach has been used for systems where one phase is a solid.[42,43] (A more elaborate ansatz has also been used for a semiconductor-vacuum system.[44]) For a system of two dielectrics, the same approach yields an obvious inconsistency in the limit where the two dielectrics have the same properties. In this case the result does not reduce to the correct limit for a single phase behavior, for which $\varepsilon(\mathbf{r}, \mathbf{r}')$ correlates all pairs of points, not just those on the same side of a now only imagined boundary. (While the important property is $\varepsilon^{-1}(r,r')$, it too would be incorrect in the cited limit, since $\varepsilon(r, r')$ is presumed to have a unique inverse.) Thus, if a continuum type nonlocal formalism for liquid-liquid systems is employed, some alternative approximation for the interfacial region would be desirable.

Acknowledgment

It is a pleasure to participate in this issue honoring Harry Drickamer, a long-time friend and colleague at Illinois. Somehow, with his love of history, it seemed appropriate to return to a subject initiated some years ago, and perhaps in his many contributions he has occasionally done the same.

Acknowledgment is made to the Office of Naval Research and to the Donors of The Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. I should like to thank B. B. Smith, C. A. Koval and N. Lewis and his students for calling my attention to some of these problems and for useful discussions.

Appendix - Derivation of Eq. (25).

We calculate here the "volume" v per unit area of interface defined as in eq. (A1) below, such that the reactant 1 lies wholly in phase 1 and reactant 2 lies wholly in phase 2. Coordinates z_1, θ, ϕ (ϕ is an angle, not shown, about the z_1-axis) and R are introduced, as in Fig. 1a. The maximum value of θ, θ_{max}, for a fixed z_1 and R corresponds to the arrangement in Fig. 1b, where reactant 2 just touches the interface. Calculation of the "volume" v involves finding all configurations of the pair, per unit area of interface, such that the conditions mentioned above are fulfilled. At fixed z_1 and R, the area element $R^2 \sin\theta\, d\theta\, d\phi$ is integrated from $\phi = 0$ to 2π and from $\theta = 0$ to $\theta_{max}(z_1, R)$. The result is then integrated at fixed R from $z_1 = a_1$, the radius of reactant 1, to the maximum value of z_1, $z_1 = R - a_2$. Then, R is integrated from $R = a_1 + a_2$ to ∞. The final result is independent of the (x, y) position along the plane, and so is a constant in the unit area. We thus have

$$v = \int_{R=a_1+a_2}^{\infty} \int_{z_1=a_1}^{R-a_2} \int_{\theta=0}^{\theta_{max}(z_1,R)} \int_{\phi=0}^{2\pi} R^2 \sin\theta\, d\phi\, d\theta\, dz_1\, dR\; k(R)/k(R_{max}) \tag{A1}$$

$$= \pi \int_{R=a_1+a_2}^{\infty} (R - a_1 - a_2)^2 R\, k(R)\, dR / k(R_{max}) \;,$$

inasmuch as $\int \sin\theta\, d\theta$ equals $1 - \cos\theta_{max}$, i.e., $1 - (z_1 + a_2)/R$. Here, $k(R)$ is a weighting factor, $\kappa(R) \exp[-\Delta G_r^{\ddagger}(R)/k_B T]$, and R_{max} is the R where this factor is a maximum. The $\kappa \exp(-\Delta G_r^{\ddagger}/k_B T)$ in eq. (26) denotes, in fact, $k(R_{max}) \exp[-\Delta G_r^{\ddagger}(R_{max})/k_B T]$. The weighting factor typically decays exponentially with distance at large R[27,45] but may even pass through a maximum[45] at an R close to $a_1 + a_2$. If, however, in eq. (A1) we let $k(R)/k(R_{max})$ equal $\exp[-(R - a_1 - a_2)/\Delta R]$ then the leading term from the R-integration in eq. (A1) leads to eq. (27). (ΔR is usually denoted in the literature by $1/\beta$).

Equation (A1) is based on a sharp boundary of the two immiscible phases. When instead there is some interpenetration of the two phases at the interface, the

θ_{max} may be larger than the value indicated in Fig. 1. For example, if the center of ion 2 can touch the interface as a result of penetration, $\cos\theta_{max}$ is z_1/R, while if the center of ion 1 can touch the interface z_1 varies from 0 to R instead of the limits indicated in eq. (A1). In this case we obtain eq. (28) as the leading term in the integration, using an exponential decay, as above.

For comparison, it is useful to recall the value of υ when there was only one reactant, instead of two, as in a metal-liquid system. Here, for a unit area of interface we would have instead of eq. (27) or (28),

$$\upsilon = \Delta R \quad . \tag{A2}$$

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19. E. g., electrical double layer effects on w^r are considered in ref. 8b.

20. In this way, dielectric image effects within the ion, due to the difference of the "dielectric constant" inside the ion and the dielectric constant of the liquid, is neglected. (cf. ref. 3, footnote 29). Strictly speaking a more detailed calculation would include such effects and also use the actual charge distribution inside the ion. In such dielectric image effects are typically small in bulk solution (e.g., Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 58).

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22. (*a*) *d* is defined (e. g., ref. 13*d*) as the distance from the charge to the "termination" of the bulk metal, the latter being a plane half-way between the

center of the outermost atomic layer and the center of the next would-be layer if the crystal were infinite. Values of d_0 from 0.64 Å to 0.85 Å were estimated in ref. 13*a*, 0.26 Å to 0.50 Å in ref. 13*b*, and 0.37 Å to 0.66 Å in ref. 13*c*, depending upon the electron density in the metal. (These results are also summarized in Table 4 of ref. 13c.) The model used in these studies entails a spillover of charge outside the $d = 0$ plane, the image charge then being situated slightly closer to the approaching charge e than is the image in the classical model, for which $d_0 = 0$. (*b*) Dietz, R. E.; McRae, E. G.; Campbell, R. L. *Phys. Rev. Lett.* **1980**, *45*, 1280. The value of d_0 was set equal to 2 Å and a linear interpolation was used to remove the unreal singularity at $d = d_0$.

23. In this model[14] there is a sharp infinite potential step, which confines the negative charge and a uniform background of positive charge (jellium model). Since the electronic wave function vanishes at the boundary the electronic charge is displaced a distance ℓ *into* the metal, in the absence of the approaching charge e, where $\ell \sim 3\pi/8k_F$, and k_F is the Fermi wave vector. In this model the image charge is displaced into the metal a mean distance of r_0 equal to $k_s^{-1} \exp(-k_s\ell)$, where k_s is the Thomas-Fermi screening parameter.[14] (It can't spill over into the vacuum in this model, because of the infinite potential step at $d = 0$.) Thereby, the denominator in eq. (21) is found to be $(d + r_0)$ instead of $d - d_0$. The values of k_F and k_s are given by $k_F = (3\pi^2 n)^{1/3}$ and $k_s^2 = 4(3n/\pi)^{1/3}/a_0$, where a_0 is 0.529 Å (Kittel, C. *Solid State Physics*, 6th ed.; Wiley: New York, 1986, pp. 246, 266). For silver as an electrode n is 0.058 $Å^{-3}$ (Smith, A. C.; Janak, J. F.; Adler, R. B. *Electronic Conduction in Solids*; McGraw-Hill: New York, 1967, p. 180) and so $k_F = 1.12$ $Å^{-1}$, $k_s = 1.70$ $Å^{-1}$ and $\ell = 0.98$ Å. r_0 then equals 0.11 Å. The $(d + r_0)^{-1}$ expression was derived for the case that $k_s d \gg 1$. In the present case, with $d \sim 3.5$ Å, $k_s d = 5.95$. (The correction using instead the integral in eq. (12) of ref. 14 is negligible.)

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25. Similarly, in the case of reaction between a single ion or molecule 1 and an interface, the corresponding rate constant k_r is normally defined via $-dN_1/dt = k_r n_1 A$, and so, conventionally, in units of cm sec^{-1}.

26. E.g., Kauzmann, W. *Quantum Chemistry*; Academic Press: New York, 1957, p. 541. The present discussion regarding time in the crossing region was motivated by the discussion there, but is done somewhat differently in the present paper.

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28. At the curve crossing there are two degenerate localized electronic states ϕ_1 and ϕ_2, one with the charge localized in one reactant, the other with the charge gone from that reactant. Each of these two states can be expressed as a linear combination of their symmetric and antisymmetric algebraic sums, namely the two adiabatic states. At the crossing the adiabatic states have an energy difference of $2H_{12}$. A system fixed at the crossing and initially the state ϕ_1, a nonstationary state, oscillates between ϕ_1 and ϕ_2 with the time to go in one-half of this cycle from ϕ_1 to ϕ_2 being the Δt given in the text.

29. The difference of slopes $s_1 - s_2$ of two potential curves, $(k/2)(q - q_0^p)^2$ and $(k/2)(q - q_0^p)^2$ is $(k/2)(q_0^p - q_0^r)$, the magnitude of which can be written as $(2k\lambda_i)^{\frac{1}{2}}$, where $\lambda_i = (1/2)(q_0^p - q_0^r)^2$. Using the fact that the vibration frequency ν equals $(2\pi)^{-1}(k/\mu)^{\frac{1}{2}}$, then replacing v_x, the velocity along the reaction coordinate, by an average value for the present purposes,

$$\int_0^{\infty} v_x \exp(-\mu v_x^2/2k_BT)\,dv_x \Big/ \int_0^{\infty} \exp(-\mu v_x^2/2k_BT)\,dv_x$$

i.e., by $(2k_BT/\pi\mu)^{\frac{1}{2}}$, and neglecting the difference between a factor $\pi^{3/2}/4$ and unity, eq. (31) is obtained. In practice, in a calculation of the rate one would, of course, integrate P itself over a Boltzmann-weighted distribution of P's (e.g., ref. 3) and not replace v_x by an average. However, in the present context we are interested, instead, only in obtaining an approximate time-scale for the "almost instantaneous" electron transfer in the transition state region.

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31. A group of fast reactions at one end of this plot do not have this slope, for reasons which are still not clear.

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39. One example is the treatment of separation distance effects in charge transfer spectra, where, a dielectric screening constant and an intramolecular λ_i were used as adjustable parameters.[38] Another example is the discrepancy between free energies of solvation of small ions and those calculated by usual electrostatics (local) using the Born charging formula. Conventionally the difference has been ascribed to dielectric saturation, and either an additional constant has been added to the ion radius or, sometimes, an innermost shell of bound solvent molecules has been assumed. As an alternative for 1:1 electrolytes a nonlocal dielectric effect was postulated and adjustable screening constants introduced.[36] However, recently Krishtalik, L. I. (40th ISE Meeting, Kyoto, Japan, 1989) reported that nonlocal solvent dielectric effects have been overestimated. He obtained, instead, good agreement for the free energies of transfer of (+ , −) pairs of metallocene ions from one solvent to another, using a local dielectric response (to be published).

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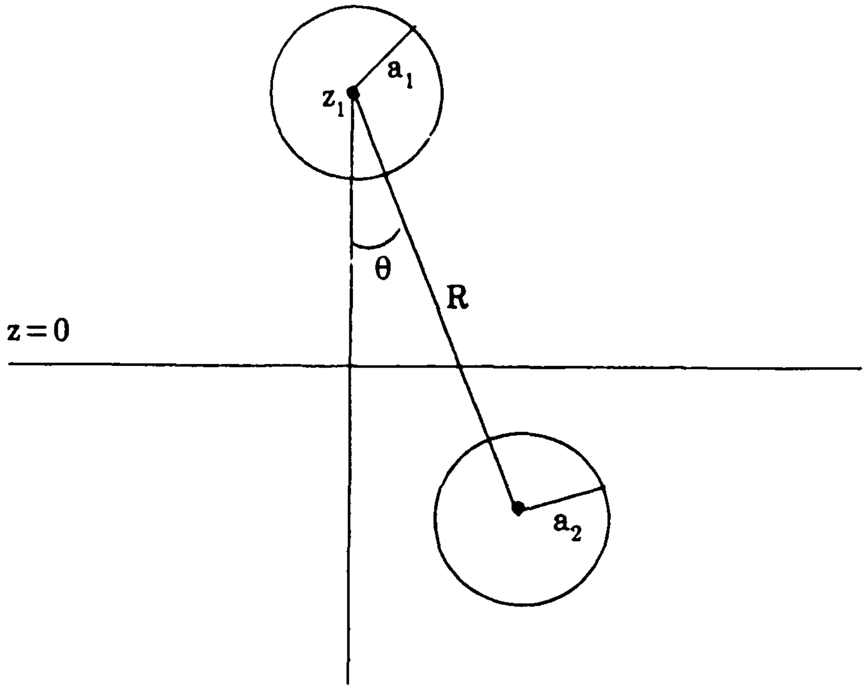
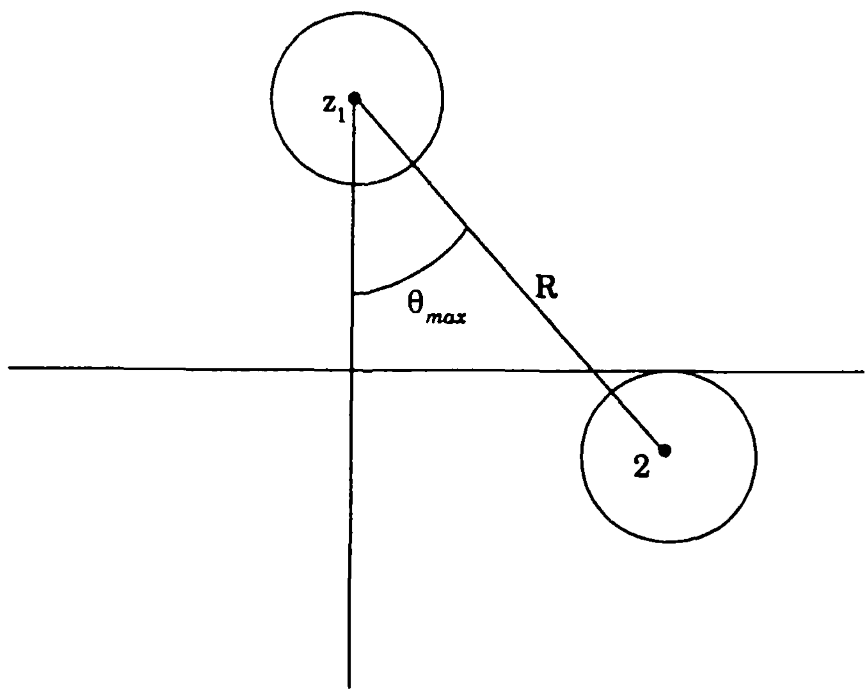
Fig. 1. (a) Coordinates for the calculation of the hypervolume υ in the Appendix and eq. (27). (b) Configuration indicating the maximum value of θ, for a given value of z_1 and of R.



(a)



(b)

Fig. 1